Historic, archived document

Do not assume content reflects current scientific knowledge, policies, or practices.

Issued August 26, 1912.

U. S. DEPARTMENT OF AGRICULTURE,

FOREST SERVICE—BULLETIN 109.

HENRY S. GRAVES, Forester.

FOREST PRODUCTS LABORATORY SERIES.

DISTILLATION OF RESINOUS WOOD BY SATURATED STEAM.

BY

L. F. HAWLEY,

Chemist in Forest Products,

AND

R. C. PALMER,

Assistant Chemical Engineer in Forest Products.

WASHINGTON:

GOVERNMENT PRINTING OFFICE.

1912.

Issued August 26, 1912.

U. S. DEPARTMENT OF AGRICULTURE,

FOREST SERVICE—BULLETIN 109.

HENRY S. GRAVES, Forester.

FOREST PRODUCTS LABORATORY SERIES.

DISTILLATION OF RESINOUS WOOD BY SATURATED STEAM.

BY

L. F. HAWLEY,

Chemist in Forest Products,

AND

R. C. PALMER,

Assistant Chemical Engineer in Forest Products.

WASHINGTON:

GOVERNMENT PRINTING OFFICE.

1912.

FOREST SERVICE.

Henry S. Graves, *Forester.*
Albert F. Potter, *Associate Forester.*
Herbert A. Smith, *Editor.*

Branch of Products.

McGarvey Cline, *Director, Forest Products Laboratory, in charge.*
Howard F. Weiss, *Assistant Director.*

WOOD DISTILLATION.

L. F. Hawley, *Chemist in Forest Products, in charge.*
E. Bateman, A. W. Schorger, *Chemists in Forest Products.*
F. W. Kressmann, R. C. Palmer, Jacob M. Johlin, Jr., *Assistant Chemists in Forest Products.*

LETTER OF TRANSMITTAL.

U. S. Department of Agriculture,
Forest Service,
Washington, D. C., March 15, 1912.

Sir: I have the honor to transmit herewith a manuscript entitled "Distillation of Resinous Wood by Saturated Steam," by L. F. Hawley, chemist in forest products, and R. C. Palmer, assistant chemical engineer in forest products, and to recommend its publication as Bulletin 109 of the Forest Service.

The investigation was carried on at the Forest Products Laboratory, maintained in cooperation with the University of Wisconsin.

Respectfully,

Henry S. Graves,
Forester.

Hon. James Wilson,
Secretary of Agriculture.

CONTENTS.

ILLUSTRATIONS.

DISTILLATION OF RESINOUS WOOD BY SATURATED STEAM.

PURPOSE OF THE STUDY.

The steam distillation process for obtaining volatile oils from the wood of longleaf pine has been the basis of a small industry since about 1903. Apparently the process was introduced in an attempt to produce wood turpentines at temperatures lower than those used in destructive distillation, and thus to obtain a product uncontaminated by the decomposition products of wood and rosin. Quite a large number of plants have been built to use either sawmill waste or lightwood, or both, but many have been abandoned, and probably not more than 15 were in operation in 1911. The quality of the crude turpentine produced usually has been very good, but because this is the only product obtained, or because the yield of this product is generally lower than that of "crude turpentines" from other processes, the plants have been successful only under especially favorable conditions.

The process seems to be very promising, however, when combined with others for the utilization of the steamed chips, as, for instance, for the extraction of the rosin with volatile solvents. The process might be favored, also, where the material would be largely used as fuel, or wasted, or where it is very cheap, or so poor in quality that more complicated processes would not be profitable. These conditions generally obtain with the waste wood of sawmills now used as fuel at the plant or burned on the rubbish pile. In these fields the steam distillation of resinous woods will undoubtedly expand.

There has been no uniformity in commercial practice nor in the opinions of the various operators as to the proper steam pressure, size of chips, or rapidity of distillation, and no experimental data have been published on the effects produced by these various, readily controlled variables. In methods described in patent specifications the greatest stress has been laid on the mechanical features of charging and discharging and of distributing the steam throughout the retort, which, although of great importance in economy of operation, throw no light on other equally important features.

There seemed to be, therefore, a profitable field for investigations to determine the relations between the conditions under which the distillation is conducted, on the one hand, and, on the other, the amount and kind of products, and the readiness with which they are obtained. The results of the investigations are set forth to help promote the expansion of the steam distillation industry, and to increase in this way the utilization of a class of material which now is wasted.

THEORETICAL CONSIDERATIONS.

In the description of the experimental work and the discussion of the results it will be necessary to refer constantly to certain theoretical principles which apply to the distillation of volatile oils with steam, and, in order to make the future discussion clearer, these principles are briefly presented.

In order to simplify the deductions, the following assumptions are made in regard to the resinous material contained in the "lightwood" from the longleaf pine:[1]

(1) It is composed only of turpentine, pine oil,[2] and rosin;

(2) The components are all simple substances completely soluble in one another;

(3) None of the components is soluble in water;

(4) The turpentine and pine oil are both volatile, but the turpentine has the lower boiling point;

(5) Rosin is nonvolatile.

While these assumptions are not strictly true in all cases, none of them is sufficiently incorrect to seriously affect the conclusions.

The following deductions can be made as to distillation of the resinous materials, defined by these assumptions, with steam:[3]

(1) There will be a separation of the two volatile constituents, with turpentine in greater proportion in the first part of the distillate and pine oil in the latter part.

(2) Under normal pressure the temperature of the distillation will be slightly above 95° C. at the beginning, and will rise throughout

---

[1] M. Vezes (Bull. Soc. Chem., **29**, 470–478, 1903) has given a very clear and complete discussion of the principles underlying the distillation of the oleoresin from the maritime pine of France. For the simplification of the discussion the following assumptions were made:

(1) That the oleoresin is composed only of essence (turpentine) and colophony (rosin);

(2) That these components are both simple substances completely soluble in each other;

(3) That neither is soluble in water; and

(4) That rosin is nonvolatile.

In regard to the oleoresin obtained by chipping the live longleaf pine tree of the United States the same assumption can be made, but the oleoresin contained in the pitchy "lightwood" from this species has another component, the heavy, high-boiling "pine oil," which must be taken into consideration in the discussion of the steam distillation of such wood.

[2] A discussion of the occurrence of pine oil in the "lightwood" of longleaf pine is given in Forest Service Bulletin 105, "Wood Turpentines, Their Analysis, Refining, and Composition," by L. F. Hawley.

[3] A detailed discussion of the methods used in making these deductions can not be given here, since a complete exposition of the laws governing the distillation of a four-component system like this would require too much space.

the distillation, never quite reaching 100° C., however, as long as any of the turpentine or pine oil remains undistilled.

(3) If the pressure is increased the temperature will be increased; the temperature depends upon the pressure and on the concentrations of the turpentine, pine oil, and rosin; it will, however, never reach the steam temperature corresponding to the pressures used as long as any turpentine or pine oil remains undistilled.

(4) The proportion of oil to water in the distillate will decrease as the distillation progresses; this proportion is influenced only by the composition of the oleoresin at various stages of the distillation.[1]

In these deductions it is considered that the system is in complete equilibrium; under such conditions the behavior of oleoresin when distilled with steam can be foretold with considerable accuracy, but in the distillation of wood containing oleoresin there is a disturbing factor which necessitates investigation of several variables (p. 18). This disturbing factor is the difficulty of keeping a complete equilibrium between the oleoresin and the steam, since the wood surrounds the oleoresin and tends to keep the steam from coming in contact with it.

The effects of the size of chips and of the rapidity of distillation and (aside from temperature changes) the effects of steam pressure are due to the influence of these factors on the completeness of equilibrium between the oleoresin and the steam, rather than to their influence on the behavior of the oleoresin and steam when completely in equilibrium.

EXPERIMENTAL METHODS.

GENERAL PROCEDURE.

The general procedure was to distill charges of the same sized chips under different conditions, and of different sized chips under identical conditions, and to note carefully the variations in the results of the distillations. It was not practicable to make all the runs on exactly comparable material, because a large number of charges of equal resin content could not be secured, and because the material could not be kept without some loss of volatile oil by evaporation. The runs were therefore made in groups with comparable material in each group; the results from each group were made comparable to some extent with those from other groups by a comparison of the resin content of the different groups. This was readily accomplished by distilling the sawdust obtained in the preparation of the material for each group, as this sawdust was a good average sample of the whole group.

[1] A change in the pressure at which the distillation is carried on might change the proportion of water to oil in the distillate, but this change would be slight and there is not sufficient information available to decide even the direction of this change.

APPARATUS.

A sketch of the retort used for the distillations is shown in figure 1. This retort was designed for use in extraction of tannin from wood and bark, as well as for distillation experiments; it was therefore made of copper and had the closed steam coils *B*. The perforated plate *C* was designed to hold up the charge while the lower head of

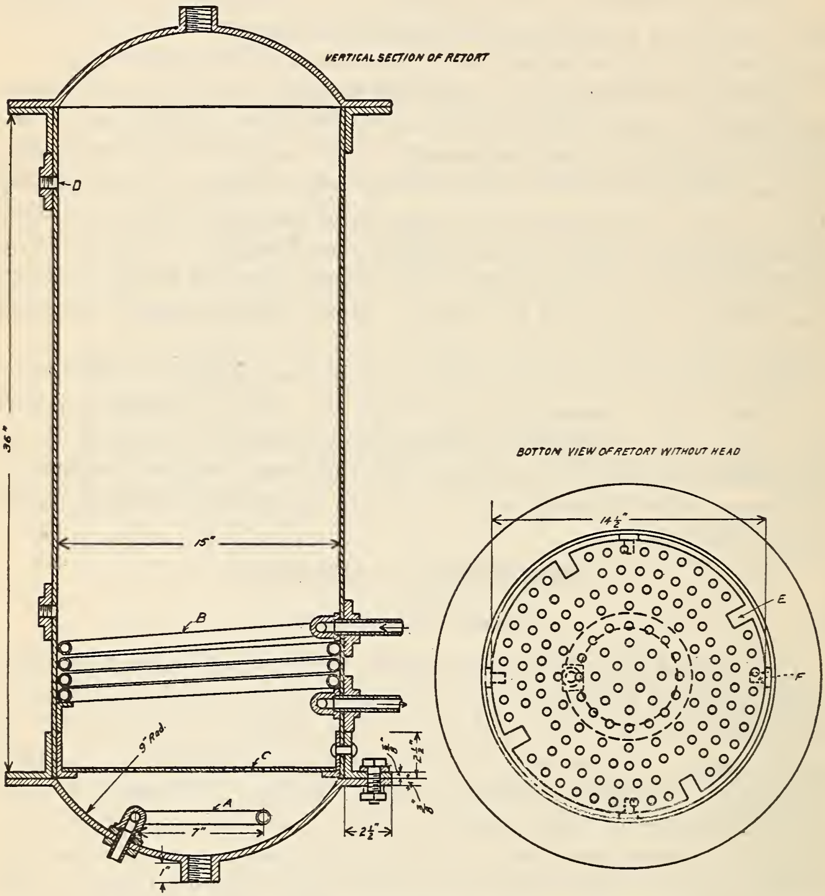

FIG. 1—Experimental retort.

the retort was taken off; then by revolving the plate until the slots *E* came opposite the supporting lugs *F*, the plate falls and the charge can be removed. The pressure gauge was attached at *D*. The other parts of the retort require no special description. An ordinary copper worm condenser was used and the distillate was caught in 1-liter graduated cylinders.

MATERIALS.

The J. G. Newman Lumber Co., of Hattiesburg, Miss., furnished for the experiments a large log of pitchy lightwood in which the pitch was distributed with unusual evenness. From this log it was possible to prepare a number of charges of chips, of which all from one portion of the log were similar in resin content.

PREPARATION OF MATERIAL.

The method of selecting material so that each charge should be comparable with the other charges in the same group is shown in Table 1 and figure 2. The sticks were sawed into sections at one time, but usually the sections were chipped only as required; that is, just before each distillation. Thus the sections for the last runs of a group had been longer cut than those of the first runs, and although they were kept in covered cans, or if without cover were piled close together, there was still some chance of loss by volatilization, especially when some time intervened, as in the large number of runs in Group I. To lessen the loss by volatilization during the chipping process, the chips were covered with water as fast as they were made. The sawdust charges were put into the retort without any delay after collection, except in runs 2 and 3, which were prepared and collected but not distilled at the same time with run 1.

DISTILLATION.

Only a brief description of the procedure needs be given here. The same general methods were used in all cases and the details are given later in the tabulated record of the runs.

REGULATION.

The speed and pressure of the distillations were regulated simply by the inlet valve at the bottom and by the outlet valve at the top of the retort. During distillation at atmospheric pressure the outlet valve was left open and the speed regulated by the inlet valve alone; but during distillation at higher pressure it was, of course, necessary to use both valves in order to keep both speed and pressure at the required values. The variation in speed was never more than one-half minute per liter of distillate, and in pressure never more than 2 pounds per square inch from the required values.

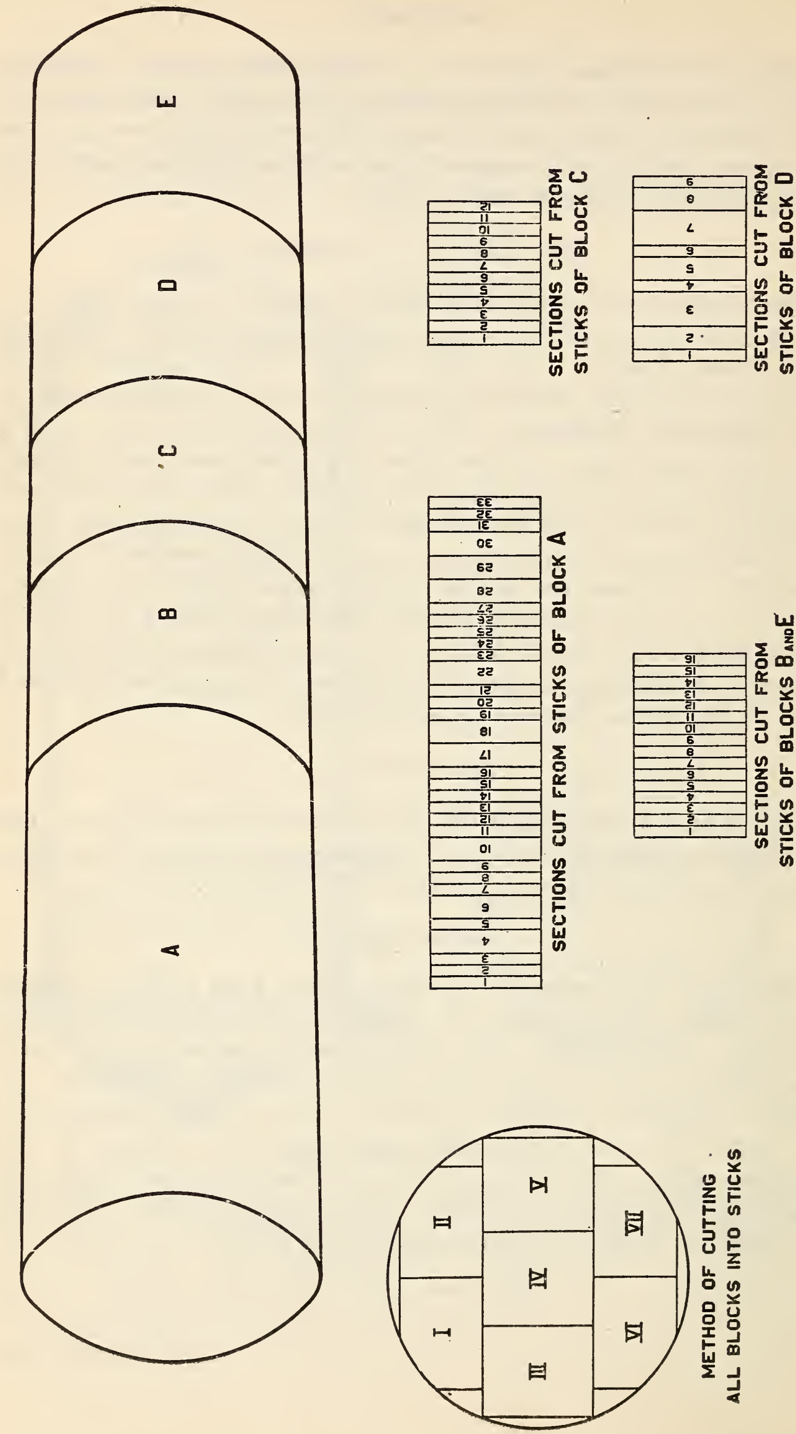

FIG. 2.—Diagram showing method of cutting up material. (In thickness the sections are drawn to scale, the smallest being 1 inch thick.)

TABLE 1.—*Experimental runs made and material used in each.*

Group No.	Run No.	Block.	Material used.			Remarks.
			Sticks.	Sections.	Size of chips.	
					Inches.	
I	1	A			Sawdust	Obtained in cutting sections.
	2	A			do	Do.
	3	A			do	Do.
	4	A	I to VII	10, 22, 28	1 x 1	
	5	A	I to VII	6, 18, 29	¼ x ⅛	
	6	A	I to VII	4, 17, 30	½ x ¼	
	7	A	I to VII	2, 14, 25	¼ x ⅛	
	8	A	I to VII	3, 5, 9, 11	¼ x ⅛	Chips from each section divided among the three runs.
	9	A		13, 15, 19, 21		
	10	A		23, 26, 27, 31		
II	11	A			Sawdust	Obtained in sawing slabs.
	12	A			1 x variable	Sections of slabs.
	13				6 x same	
III	14	A	I to VII	1, 7, 8, 12, 16	1/32 of section	One-half of each section used in each run.
	15	A	I to VII	20, 24, 32, 33	½ of section	
IV	16	B			Sawdust	Obtained in cutting sections.
	17	B	I to VII	All odd numbers	¼ x ⅛	Chips from each section divided between each run.
	18	B	I to VII			
	19	B	I to VII	All even numbers	½ x ½	Do.
	20	B	I to VII			
V	21	C			Sawdust	Obtained in cutting sections.
	22	C	I, IV, VII III, VI II, V	1, 4, 7, 10 2, 5, 8, 11 3, 6, 9, 12	2 x 2	
	23	C	III, VI II, V I, IV, VII	1, 4, 7, 10 2, 5, 8, 11 3, 6, 9, 12	2 x 2	
	24		II, V I, IV, VII III, VI	1, 4, 7, 10 2, 5, 8, 11 3, 6, 9, 12	4 x 4	
VI	25	D			Sawdust	Obtained in cutting sections and in slabbing blocks.
	26	D	I to VIII	1, 4, 6, 9	1 x 1	Obtained in cutting sections.
	27	D	I to VIII	2, 5, 8	1 x 1	
	28	D	I to VIII	3, 7	1 x 1	
VII	29	E			Sawdust	
	30	E	I, V II, VI III, VII IV	1, 5, 9, 13 4, 8, 12, 16 3, 7, 11, 15 2, 6, 10, 14	Shavings	
	31	E	I, V II, VI III, VII IV	3, 7, 11, 15 2, 6, 10, 14 1, 5, 9, 13 4, 8, 12, 16	do	
	32	E	II, V II, VI III, VII IV	2, 6, 10, 14 1, 5, 9, 13 4, 8, 12, 16 3, 7, 11, 15	½ x ½	
	33	E	I, V II, VI II, VII IV	4, 8, 12, 16 3, 7, 11, 15 2, 6, 10, 14 1, 5, 9, 13	½ x ½	

DATA OBTAINED.

A typical data sheet which gives the records obtained in one distillation is shown in Table 2. The distillate was caught in 1-liter fractions and the time and pressure were recorded with every fraction. The amount of oil in each liter of distillate was determined as accurately as possible in the original receiver—a 1-liter cylinder graduated to 10 cubic centimeters; the oil was then separated from the water in a separatory funnel and its specific gravity determined. When the amount of oil in a single fraction was so small that the

specific gravity could not readily be determined, the oil was combined from a number of fractions. As a check, the combined oil from all the fractions, or from the fractions of certain portions of the distillation, was accurately measured.

Only the essential parts of the operations are presented, with computations derived from them. The discussion will be given after the experimental work has been described.

END POINT.

It will be noticed in Table 2 that the amount of oil in 1 liter of distillate progressively decreased, but this decrease was very slow toward the end of a distillation. It became necessary, therefore, to arbitrarily fix upon that ratio of oil to water which might be considered as the end of a distillation under a given set of conditions in order that the results of various distillations might be comparable and might be completed within practicable time limits. In the first five runs this end point was too high and too variable; when these runs were made it was not recognized that the end point must be carefully regulated. These first five runs are therefore not comparable with those which follow, in which the end point was kept at somewhat lower values. A charge distilled under one set of conditions until a certain end point was reached, if interrupted for an hour or more and then continued under the same conditions, produced a further supply of oil before the same end point was reached again. This additional oil amounted to from 2 per cent to 18.8 per cent of that which had been obtained before the distillation was interrupted. The greatest increases in yields due to this manipulation were in those runs in which there was still considerable oil present in the wood when the distillation was interrupted, although, of course, all the oil that could have been removed under the existing conditions had been extracted. For instance, in runs 14 and 15, after all possible oil had been distilled at 50 pounds pressure, interruption of the distillations overnight resulted in 18.8 per cent more oil in run 14 and 15.1 per cent more in run 15 under the same conditions; and in both these cases there was still considerable oil present in the wood, as shown by further distillation at increased pressures. In runs 11 and 21, however, after all possible oil had been distilled at atmospheric pressure, interruption of the distillation secured only 2.9 per cent and 4 per cent more under the same conditions; in these cases there were much smaller quantities of oil left in the wood than in runs 14 and 15.

After run 5 the proper end point for any distillation was considered to be reached only when the required ratio of oil to water in the distillate had been attained, both before and after interruption of the distillation.

TABLE 2.—*Typical data sheet, illustrating the records taken of the distillations.*

[Project 123—Run No. 23. Chips 1″ x 2″ x 2″.]

Weight of can+water........................ 160 lbs. Steam turned on........................... 9.23
Weight of can+water+chips................ 215 lbs. Distillate began to flow.................. 9.28–30
Weight of chips............................ 55 lbs.

Time.	Distillate.	Oil in distillate.	Oil total computed.	Oil total determined.	Specific gravity of oil.	Pressure.
a. m.	*Liters.*	*c. c.*	*c. c.*	*c. c.*		*Pounds.*
9.36	1	88	88	....	0.8810	70
9.48	2	154	242	....	.8794	72
9.59½	3	110	352	362	.8851	71
10.08	4	73	425	....	....	71
10.17	5	60	485	....	.8944	68
10.29½	6	55	540	....	....	71
10.40½	7	50	590	....	.8980	70
10.51½	8	44	634	....	....	72
11.00½	9	39	673	....	.8981	70
11.08½	10	24	697	....	....	69
11.18½	11	27	724	....	.9010	72
11.28	12	26	750	....	....	69
11.38	13	19	769	....	....	72
11.47½	14	22	791	....	....	68
11.57½	15	17	808	....	.9016	69
P. M.						
12.07	16	17	825	839	....	69
12.17	17	16	841	....	....	69
12.27½	18	16	857	....	.8987	72
12.38½	19	18	875	....	....	72
12.50	20	19	894	....	....	64
1.00	21	15	909	....	....	71
1.09	22	13	922	....	.8965	72
1.18½	23	11	933	....	....	71
1.27½	24	10	943	....	....	69
1.39	25	12	955	979	....	68
1.48	26	10	965	....	....	70
2.00	27	11	976	....	....	70
2.11½	28	10	986	....	.8958	68
2.23½	29	12	998	....	....	72
2.34½	30	8	1,006	....	....	73
2.45½	31	8	1,016	1,047	....	72
2.56½	32	10	1,026	....	....	63
3.07½	33	13	1,039	....	....	45
3.17	34	6	1,045	....	....	32
3.26½	35	5	1,050	....	.8936	20
3.37	36	4	1,054	....	....	12
3.43	37	1	1,055	....	....	4
3.45	38	1	1,056	1,095	....	0
A. M.		Distillation interrupted overnight.				
9.23½	39	22	1,078	....	....	72
9.35	40	17	1,095	....	.8934	73
9.46	41	15	1,110	....	....	71
9.57	42	10	1,120	....	....	72
10.08	43	9	1,129	....	....	70
10.19	44	8	1,137	....	.9003	72
10.30	45	7	1,143	....	....	58
10.43	46	15	1,158	....	....	34
10.53	47	8	1,166	....	....	19
11.04	48	6	1,172	....	.8935	6
11.06	49	2	1,174	1,235	....	0

No. of liters.	Yield per pound.	Efficiency.
	cc.	
16	15.3	0.95
25	17.8	.71
38	19.9	.51
49	22.4	.46

Table 3.—*Summary of experimental runs.*

Group No.	Run No.	Size of chip.	0 pounds pressure.		20 and 30 pounds pressure.		40 and 50 pounds pressure.	
			Yield per pound.	Efficiency.	Yield per pound.	Efficiency.	Yield per pound.	Efficiency.
		Inches.	*c. c.*		*c. c.*		*c. c.*	
I	1	Sawdust	20.6	1.71			*c* 9.9	0.45
	2	do					*c* 32.7	1.26
	3	do	12.5	1.56			*c* 8.2	.41
	4	2 x 1 x 1						
	5	2 x ¼ x ⅛	6.4	.61	*a* 5.8	0.45	*c* 3.9	.33
	6	2 x ½ x ¼	8.0	.55	*a* 5.1	.28	*c* 6.1	.24
	7	1 x ¼ x ⅛	15.7	.63	*a* 4.6	.29	*c* 5.3	.24
	8	1 x ½ x ¼	10.2	.46	*a* 6.5	.25	*c* 6.2	.19
	9	1 x ½ x ¼			*b* 22.4	.46	*d* 3.0	.19
	10	1 x ½ x ¼					*d* 27.2	.46
II	11	Sawdust	27.7	1.46			*c* 2.0	.25
	12	1 x variable						
	13	6 x variable						
III	14	1 x 5 x 8					*d* 19.7	.35
	15	1 x ½ x 1½					*d* 24.5	.41
IV	16	Sawdust	25.2	.97			*c* 4.0	.31
	17	1 x ¼ x ⅛			*b* 24.5	.50		
	18	1 x ¼ x ⅛					*d* 26.8	.50
	19	1 x ½ x ½					*d* 25.3	.55
	20	1 x ½ x ½						
V	21	Sawdust	24.0	1.05			*c* 1.7	.23
	22	1 x 2 x 2						
	23	1 x 2 x 2						
	24	1 x 4 x 4						
VI	25	Sawdust	24.0	.89			*c* 2.6	.26
	26	1 x 1 x 1						
	27	2 x 1 x 1						
	28	3 x 1 x 1						
	29	Sawdust	19.3	.84			*c* 1.7	.17
			18.8	.94				
			.6					
	30	Shavings	19.4	.85				
							c 3.1	.39
			16.0	.84				
			1.4					
VII	31	do	17.4	.70				
							c 3.8	.38
	32	1 x ½ x ½						
	33	1 x ½ x ½						

a=20 pounds. *b*=30 pounds. *c*=40 pounds. *d*=50 pounds.

TABLE 3.—*Summary of experimental runs*—Continued.

Group No.	Run No.	Size of chip.	70 pounds pressure.		Total pressure.		Speed per liter.	End point per liter.
			Yield per pound.	Efficiency.	Yield per pound.	Efficiency.		
		Inches.	*c. c.*		*c. c.*		*Min.*	*c. c.*
I	1	Sawdust			30.5	0.90	4	25 and 12
	2	do			32.7	1.26	4	18
	3	do			20.7	.74	4	17 and 12
	4	2 x 1 x 1	20.3	0.33	20.3	.33	5	12
	5	2 x 1/4 x 1/8	9.1	.33	25.2	.38	4	12
	6	2 x 1/2 x 1/4			19.2	.34	10	10
	7	1 x 1/4 x 1/8			25.6	.40	10	10
	8	1 x 1/2 x 1/4			23.0	.29	10	10
	9	1 x 1/2 x 1/4	4.5	.21	29.9	.34	10	10
	10	1 x 1/2 x 1/4	1.5	.12	28.7	.40	10	10
II	11	Sawdust			29.7	1.10	10	10
	12	1 x variable	25.7	.49	25.7	.49	10	10
	13	6 x variable	12.3	.29	12.3	.29	10	10
III	14	1 x 5 x 8	5.9	.17	25.6	.28	10	10
	15	1 x 1/2 x 1 1/2	4.7	.15	29.2	.32	10	10
IV	16	Sawdust			29.1	.75	10	10
	17	1 x 1/4 x 1/8					10	10
	18	1 x 1/4 x 1/8					10	10
	19	1 x 1/2 x 1/2					10	10
	20	1 x 1/2 x 1/2	29.8	.63	29.8	.63	10	10
V	21	Sawdust			26.3	.82	10	10
	22	1 x 2 x 2	23.1	.39	23.1	.39	10	10
	23	1 x 2 x 2	22.4	.46	22.4	.46	10	10
	24	1 x 4 x 4	23.6	.44	23.8	.44	10	10
VI	25	Sawdust			26.6	.70	10	10
	26	1 x 1 x 1	22.8	.45	22.8	.45	10	10
	27	2 x 1 x 1	21.4	.31	21.4	.31	10	10
	28	3 x 1 x 1	12.9	.29	12.9	.29	10	10
	29	Sawdust			21.0	.64	10	10
	30	Shavings					6	5
							10	7
							6 and 10	5 and 7
							10	10
					22.5	.73	6 and 10	5 and 7
VII	31	do					3	5
							10	7
							3 and 10	5 and 7
							10	10
					21.2	.60	3 and 10	5 and 7
	32	1 x 1/2 x 1/2	20.1	.43			6	5
			.7				10	7
			20.8	.39	20.8	.39	6 and 10	5 and 7
	33	1 x 1/2 x 1/2	18.1	.39			3	5
			2.2				10	7
			20.3	.33	20.3	.33	3 and 10	5 and 7

DISCUSSION OF RESULTS.

Table 3 gives the conditions of the distillations and the results obtained. Under "Size of chip" the length parallel to the grain is given first. The probable error in the determinations of yields is apparently about 6 or 7 per cent and is due to difficulties in sampling, in regulating evaporation during the preparation of material, and in obtaining comparable end points in different distillations. An example of results which must be due to such errors is seen in runs 23 and 24. The chips in run 24 are larger than those in run 23, and the yield probably should be less, and certainly not greater, from the larger chips; yet the yields obtained from run 23 are 5 per cent less than those from run 24. A similar example is shown in runs 30 and 31. It might be thought that some of these variations in yields were due to incomplete distillation caused by the steam "channeling" through the charge in such a way that it never touched part of the wood; but in several runs, after all possible oil had been distilled under one set of conditions, the top of the retort was removed, the charge was well stirred, and the distillation continued under the same conditions as before, without any indications that the stirring had discovered undistilled material. It seems probable, therefore, that with a retort of the shape and size used the effect of incomplete distillation due to incomplete contact between the steam and the chips is negligible.

The values given under "Efficiency" are obtained by dividing the yields per pound of wood by the number of liters of total distillate, the efficiency factor being cubic centimeter of oil per pound of wood per liter of distillate, or $\frac{\text{c.c. oil}}{\text{pounds wood} \times \text{liters distillate}}$. It might be thought that this "efficiency factor" would have more significance if it represented only the relation between oil and total distillate; but, as will be seen later,[1] this relation would be affected by the quantity of wood distilled. Of course the effect may not be in exact proportion to the quantity of wood, but it is probable that more nearly comparable efficiency factors are obtained by including it. These factors represent approximately the relative quantities of oil obtained in the various runs per unit of steam consumed, and of course exclude the steam which supplies the heat losses from other causes, such as radiation.

EFFECT OF SIZE OF CHIP ON YIELD AND EFFICIENCY.

In general, the smaller the chip the larger the yields and the higher the efficiency. This is shown in Table 4, which contains selected data from Table 3. Four groups of distillations are given, in each

[1] The reasoning given on page 19 regarding the effect of the size of retort on efficiency applies also to the effect of the amount of wood on efficiency.

of which all conditions except size of chips are, as nearly as possible, the same; in every case the smaller sized chips show the larger yield and higher efficiency. The effect on yield is not so marked in the case of runs 26 and 27 (and some of the other runs given in Table 3), but this is because the pressure was so high that nearly all the oil was removed even from the larger sized chips. Of two runs in which all the oil was removed even from the larger chips, the yields would, of course, be the same, but the efficiency would probably be higher with the smaller sized chips.

EFFECT OF PRESSURE ON YIELD AND EFFICIENCY.

In general, higher pressures give larger yields without lowering the efficiency. This is shown in Table 5, which gives three groups of runs, in each of which all conditions except steam pressure are as nearly similar as possible. In all cases the higher steam pressure produced the larger yield, with equal or greater efficiency. The effect of pressure on yields is also shown in another way in many of the runs in Table 3, in which, after obtaining all possible oil under one pressure, a further yield was obtained by continuing the distillation under a higher pressure.

EFFECT OF SPEED OF DISTILLATION ON YIELD AND EFFICIENCY.

Increased speed of distillation decreases both yield and efficiency. This is shown clearly in Table 6, which gives the results of two sets of two runs each, in both of which all conditions except speed were identical. It is probable that with the rapid passage of steam through the charge it is less completely saturated with oil vapors, and this directly decreases the efficiency. With this less complete saturation, the end point is reached sooner, and this, too, probably decreases the yield. This is indicated by the more nearly equal total yields obtained by finishing up the distillations at the same pressure but at lower speeds. However, the variation in efficiency is not proportional to the speed, since doubling the speed decreases the efficiency by only about 10 per cent—from 0.94 to 0.84 in runs 30 and 31 and from 0.43 to 0.39 in runs 32 and 33.

If, as seems probable, the effects of speed are due to the variations in the time during which the steam is in contact with the wood, then the size of the retort would have a similar effect; that is, a speed of 10 minutes per liter in a retort of a given size would be equivalent to 5 minutes per liter in a retort twice as large, since a unit of steam would be in contact with a unit of wood for the same length of time in either case.

TABLE 4.—*Effect of size of chip on yield and efficiency.*

Run.	Size of chip.	Pressure.	Yield.	Efficiency.	Speed per liter.	End point oil per liter of distillate.
	Inches.	*Pounds.*	*c. c. per lb.*		*Min.*	*c. c.*
7	1 x ¼ x ⅛	(1)	15.7	0.63	10	10
8	1 x ½ x ¼		10.2	.46		
12	1-inch sections from slab	70	25.7	.49	10	10
13	6-inch sections from same		12.3	.29		
14	1 x 5 x 8	50	19.7	.35	10	10
15	1 x 1½ x 1½		24.5	.41		
26	1 x 1 x 1	70	22.8	.45	10	10
27	2 x 1 x 1		21.4	.31		
28	3 x 1 x 1		12.9	.29		

[1] Atmospheric.

TABLE 5.—*Effect of pressure on yield and efficiency.*

Run.	Size of chip.	Pressure.	Yield.	Efficiency.	Speed per liter.	End point oil per liter of distillate.
	Inches.	*Pounds.*	*c. c. per lb.*		*Min.*	*c. c.*
8	1 x ½ x ¼	(1)	10.2	0.46	10	10
9	1 x ½ x ¼	30	22.4	.46	10	10
10	1 x ½ x ¼	50	27.2	.46	10	10
17	1 x ¼ x ⅛	30	24.5	.50	10	10
18	1 x ¼ x ⅛	50	26.8	.50	10	10
19	1 x ½ x ½	50	25.3	.55	10	10
20	1 x ½ x ½	70	29.8	.63	10	10

[1] Atmospheric.

TABLE 6.—*Effect of speed on yield and efficiency.*

Run.	Size of material	Pressure.	Speed per liter.	End point oil per liter.	Yield.	Total yield.	Efficiency.	Total efficiency.
	Inches.	*Pounds.*	*Min.*	*c. c.*	*c. c. per lb.*	*c. c.*		
30	Shavings	(1)	6	5	18.8	18.8	0.94	0.94
		(1)	10	7	.6	19.4	....	.85
		40	10	10	3.1	22.5	.39	.73
31	....do	(1)	3	5	16.0	16.0	.84	.84
		(1)	10	7	1.4	17.4	....	.70
		40	10	10	3.8	21.2	.38	.60
32	1 x ½ x ½	70	6	5	20.1	20.1	.43	.43
			10	7	.7	20.8	....	.39
33	1 x ½ x ½	70	3	5	18.1	18.1	.39	.39
			10	7	2.2	20.3	....	.33

[1] Atmospheric.

RELATIONS BETWEEN END POINT, YIELD, AND EFFICIENCY.

Table 2 shows that the amount of oil in a liter of total distillate is greatest at the beginning and decreases steadily as the distillation progresses, except when conditions are changed, and then the increase in the amount of oil per liter is usually only slight and temporary. This was true in all the distillations. It is evident, therefore, that the efficiency factor will decrease steadily throughout the distillation, and its final value will depend on the end point used. Thus, the efficiency can be increased by stopping the distillation before all the oil has been obtained, but this decreases the total yield of oil. On the other hand, the efficiency will be decreased by continuing the distillation until all possible oil has been obtained, although the total yield of oil is increased. For instance, in run No. 23 (Table 3), if the distillation had been stopped with an end point of 12 c. c. per liter, at the twenty-fifth liter the yield would have been only 15.3 c. c. per pound while the efficiency would have been 0.95. By continuing the distillation until the end point (after an interruption of the distillation) was 10 c. c. per liter, the yield was much larger, 22.4 c. c. per pound, but the efficiency was only 0.46.

THE PRESSURE REQUIRED TO DISTILL COMPLETELY DIFFERENT SIZES OF MATERIAL.

SAWDUST.

The volatile oil can not be completely distilled at atmospheric pressure even from a material as finely divided as sawdust. This can be seen from runs 11, 16, 21, 25, and 29, in which, after removing all possible oil at atmospheric pressure, a further distillation at 40 pounds pressure removed from 6.6 to 15.8 per cent more oil. After distillation at 40 pounds a further distillation at 70 pounds was without appreciable results. It can be safely stated that a pressure of 40 pounds is sufficient to remove all the volatile oil from material as small as sawdust. It is possible that lower pressures might give almost as good results, but this can not be determined from the data on hand.

CHIPS 1 INCH $\times$ $\frac{1}{4}$ INCH $\times$ $\frac{1}{8}$ INCH.

This size material can not be completely distilled at 30 pounds pressure (run 17) and probably not at 50 pounds pressure (run 18). In run 18, the yield obtained from chips 1 inch $\times$ $\frac{1}{4}$ inch $\times$ $\frac{1}{8}$ inch is almost the same, within the limit of possible variation, as from the sawdust of run 16, but apparently not quite all the oil has been removed.

CHIPS 1 INCH $\times$ $\frac{1}{2}$ INCH $\times$ $\frac{1}{2}$ INCH.

Chips of this size can not be completely distilled at 50 pounds pressure (run 19), but can at 70 pounds (runs 20, 32, and 33).

CHIPS LARGER THAN 1 INCH × ½ INCH × ½ INCH.

At the maximum pressure used, 70 pounds, chips larger than 1 inch × ½ inch × ½ inch can not be completely distilled, but as the size of chips is increased there is no sudden drop in the yields obtainable at this pressure until sizes larger than 2 inches with the grain (runs 27 and 28) [1] and 4 by 4 inches across the grain are used (runs 14 and 24). It is probable that from 80 to 85 per cent of the oil could be removed from chips 2 inches × 4 inches × 4 inches by distillation at 70 pounds pressure.

EFFECT OF PRESSURE ON COMPOSITION OF OIL.

Analyses were made by the method described in Bulletin 105 [2] of part or all of the oil from each of the runs, but there was so little difference between the various samples that all of the analyses need not be given, and only a few distillation curves, which show the main points of interest, are presented.

PINE OIL.

The proportion of pine oil in the crude turpentine did not vary, except in cases which could be explained by variation in other factors besides pressure, and therefore, so far as the results show, the pressure has no influence on the proportion of pine oil except the influence due to increasing the total yields. That is, the pine oil has a higher boiling point, and therefore would be removed last, giving a higher proportion of pine oil in those cases in which the yield is greater. In all cases where the total oil obtained was analyzed and where the oil was nearly completely removed from the wood the percentage of pine oil by weight varied only between 48 per cent and 52 per cent.[3] In cases where only part of the oil was removed by the distillation, as in run 4, the proportion of pine oil was less.

---

[1] In determining the percentage of total oil obtained in the runs of Group VI it must be remembered that the sawdust of run 25 was not exactly a representative sample of the material of that group, but that it was mixed with the sawdust obtained in cutting the slabs from the blocks. (See Table 1.) In several cases similar samples of sawdust obtained in cutting the slabs had been distilled and found to contain more volatile oil than the sawdust obtained in cutting the blocks. It is probable, therefore, that the proportion of volatile oil in the mixed sample of sawdust was somewhat greater than in the rest of the material in this group. This point is further indicated by a comparison of the yields obtained from the sawdust runs in the different groups. With the exception of Group VI (run 25) the yields from the sawdust decrease, as might be expected, for the reason that the material for the groups was cut from the same log in order of the group number, beginning at the butt end, and the content of volatile oil in the butt end was higher than in the upper portions of the log. It is probable, therefore, that a value of from 24 to 25 c. c. of oil per pound of wood would more nearly represent the volatile oil content of the group.

[2] Bulletin 105, Forest Service, U. S. Department of Agriculture, "Wood Turpentines, Their Analysis, Distillation, and Composition."

[3] Exceptions were found to this in the oils from Group II, which contained about 28 per cent pine oil, but the material for this group did not represent a complete cross section of the log, being composed instead only of the outside pieces, the slabs. The outer layers of this log evidently contained a smaller proportion of pine oil than the rest of the wood.

DIPENTENE.

The detection of small differences in the proportion of dipentene present can not be made by the method of examination used, especially when such large proportions of pine oil are present. There seemed to be, however, more dipentene in the crude turpentines pro-

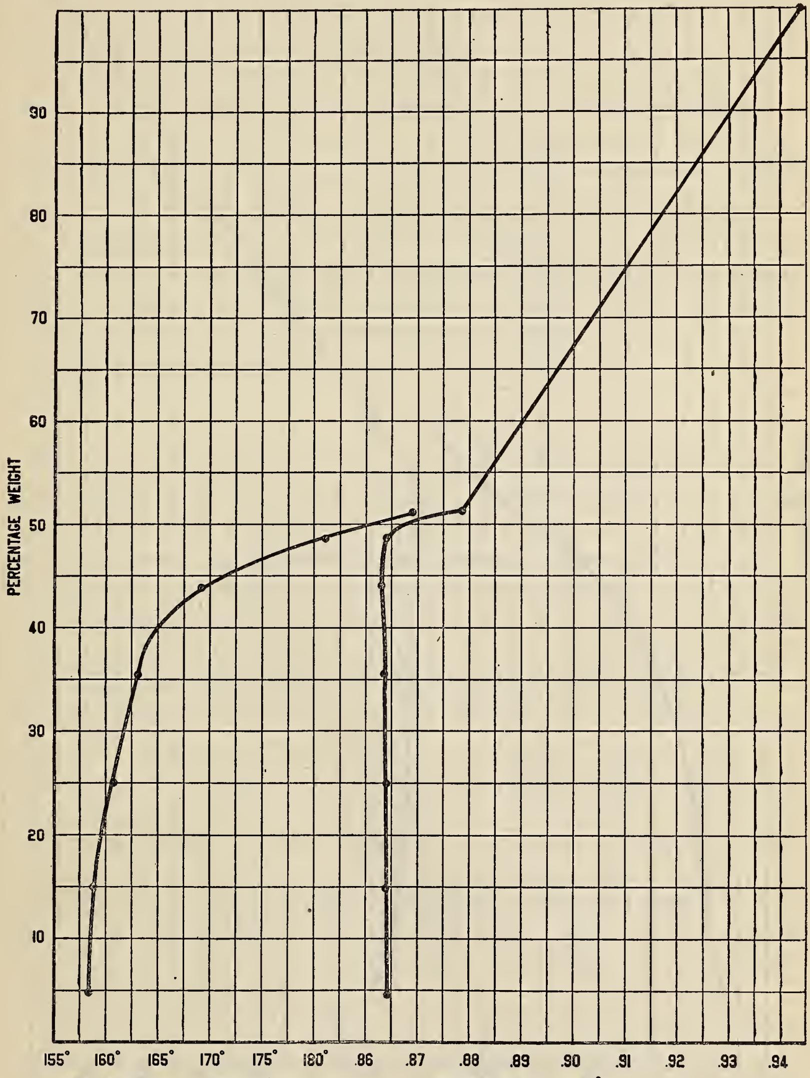

FIG. 3.—Boiling-point and specific-gravity curves for oil from run 21.

duced at higher pressures. Figures 3 and 4, representing the distillation curves obtained in the analyses of the oils from runs 21 and 23, respectively, illustrate this point. The oil obtained mostly at atmospheric pressure from sawdust (fig. 3) apparently contains less

dipentene than the oil distilled entirely at 70 pounds pressure (fig. 4); in the latter case the specific gravity values are lower and the proportion of the oil boiling between 165° and 180° is larger. Formerly it

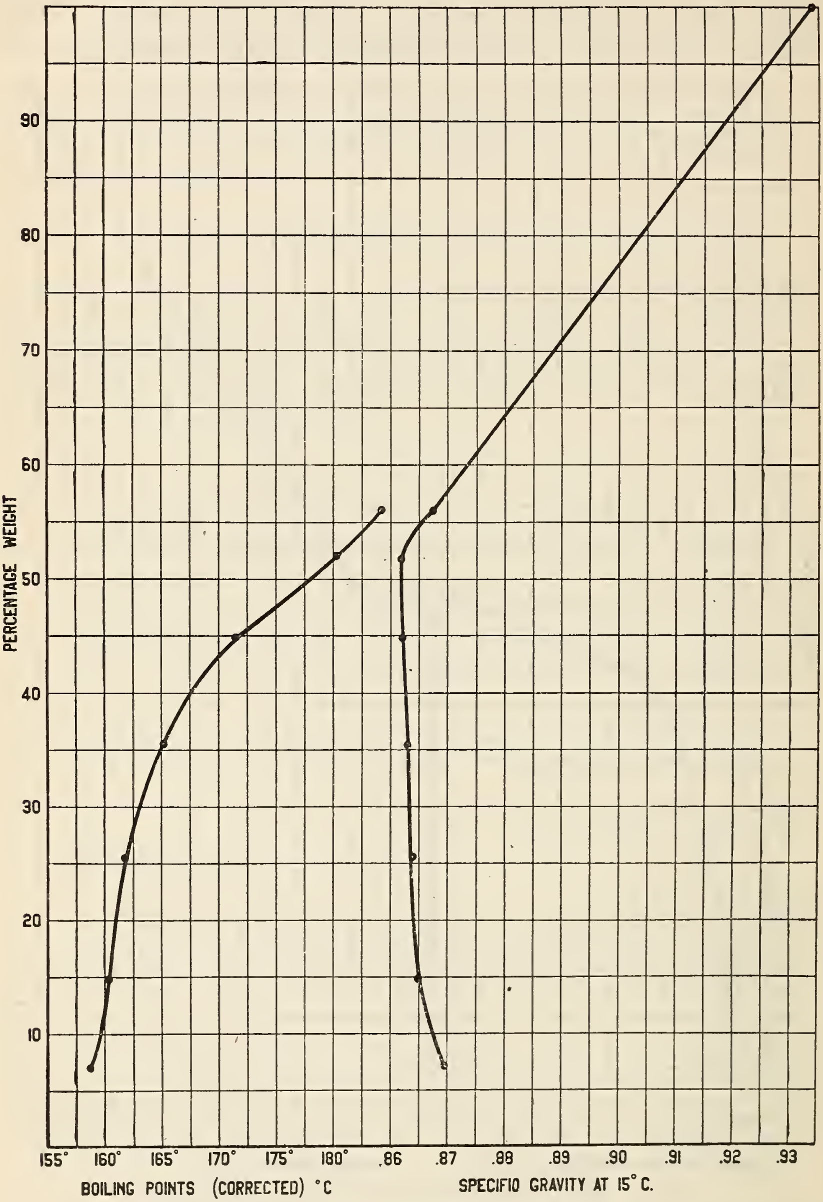

FIG. 4.—Boiling-point and specific-gravity curves for oil from run 23.

was thought that the dipentene in wood turpentines was caused by the temperature used in distilling the oil from the wood, but indications of dipentene were found in all the samples of oil obtained in this

investigation, even in those produced at atmospheric pressure, and it is very probable that dipentene was present, as such, in the wood. In order to make sure that this material with low specific gravity and high boiling point was dipentene and not some other terpene with similar physical properties, a chemical examination was made of the fractions from 165° to 185° from some of the turpentines produced at atmospheric pressure and dipentene was identified by means of the tetrabromide, m. p., 125°–126°.

In order to determine the possibility of the transformation of pinene into dipentene under the condition of steam distillation, the sawdust from run 29 was air dried and moistened with 1,175 c. c. of gum turpentine (an amount equal to the total volatile oil originally present) and then distilled at atmospheric pressure. The resultant oil, on analysis, showed no indications of dipentene. The experiment was repeated, making the distillation at 50 pounds pressure, but with the same result. These results preclude the possibility of a formation of dipentene from pinene at 50 pounds pressure or less, and indicate strongly that dipentene occurs, as such, in lightwood.

LIGHT OILS.

Figures 3 and 4 also illustrate another effect of pressure on the composition of the crude turpentines. In these analyses, as in many others, the crude turpentines produced at pressures as high as 70 pounds show a considerably higher value for the specific gravity of the first fraction than do the turpentines produced at lower pressures. This indicates that some substance with low boiling point and high gravity (above 0.870 at 15° C.) is produced at the higher pressures; this substance might come from the incipient stage of a decomposition of some portion of the resin at the temperature to which it is subjected. The first fractions from the analyses which contained this substance were slightly yellow and had a peculiar odor. A treatment with caustic soda reduced the gravity of these fractions but deepened the yellow color. It was found, however, that by the caustic-soda treatment of a turpentine such as that shown in figure 3, followed by a distillation, it was possible to prepare a refined turpentine which showed no abnormality of the first fraction in color, odor, or gravity. The presence of this substance should not, therefore, introduce any difficulty in the refining process.

Another test for the presence of decomposition products was made on several of the samples produced at different pressures by treating the oil with concentrated hydrochloric acid. A red color produced in this way is supposed to indicate the presence of rosin oil. There was only a very slight coloration of the oils produced at atmospheric pressure, but this coloration increased with the pressure, becoming very marked in the oils produced at 50 and at 70 pounds pressure.

FRACTIONATION OF THE OIL DURING DISTILLATION.

Some very interesting conclusions as to the manner in which the volatile oil leaves the wood can be obtained by comparing the values of the specific gravity of various portions of the distillate. As previously stated, the specific gravity of the oil was determined from each liter of distillate or from as many liters as were necessary to furnish the amount of oil required for a determination. Figures 5, 6, and 7 show these values of the specific gravity obtained in runs 16, 20, and 7, respectively, plotted against the percentages of the total oil obtained.

Figure 5 shows the changes in the specific gravity of the oil obtained during the distillation of a charge of sawdust, first at atmospheric pressure, and then at 40 pounds pressure. The first portions of the oil were nearly pure turpentine, but after about 44 per cent had been distilled the gravity increased rapidly, indicating the presence of pine oil in increasing quantities; when the distillation was from about 67 per cent to 83 per cent complete, the oil was nearly pure pine oil. The part of the curve up to 83 per cent resembles very closely a curve obtained from the steam distillation of a crude turpentine; that is, the presence or absence of the wood seems to have no effect on the manner in which the volatile oils are distilled. A difference is seen, however, in that portion of the curve beyond 83 per cent; after practically all possible oil has been removed by a continuous distillation at atmospheric pressure, interruption of the distillation, followed by a further distillation under the same pressure, produced a small further yield of oil with a lower gravity, and, on increasing the steam pressure, still more oil was obtained with a still lower gravity. This indicates that both the interruption of the distillation and the increase in steam pressure brought more oil into contact with the steam and that this oil contained some of the low-gravity turpentine material.

A very different behavior is shown in figure 6, which represents the distillation of chips 1 inch$\times\frac{1}{2}$ inch$\times\frac{1}{2}$ inch at a pressure of 70 pounds. In distillation under these conditions there was much less tendency for the oil to be separated as distilled, the gravity of the very first fraction being higher than that of pure turpentine and the gravity of the later fractions never reaching that of pure pine oil; that is, the turpentine and pine oil distilled together throughout the run. This indicates that new supplies of volatile oils were brought into contact with the steam more or less continuously throughout the distillation; had it been otherwise the turpentine would have distilled first and the last fractions would have been nearly pure pine oil.

A still more striking picture of the variation in the gravity of the distillate due to changes in the conditions of distillation is shown in

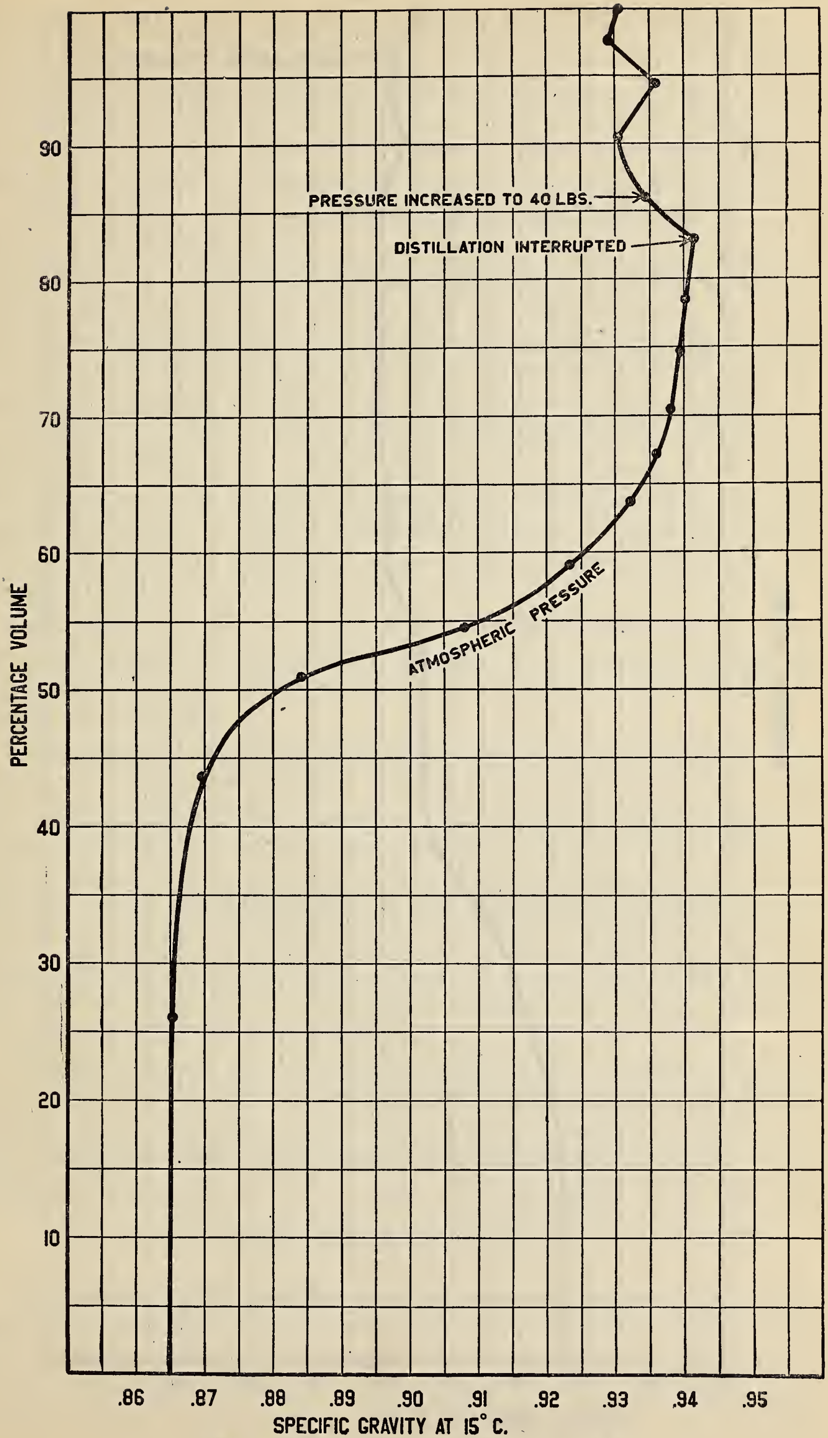

Fig. 5.—Curve showing fractionation of oil during run 16.

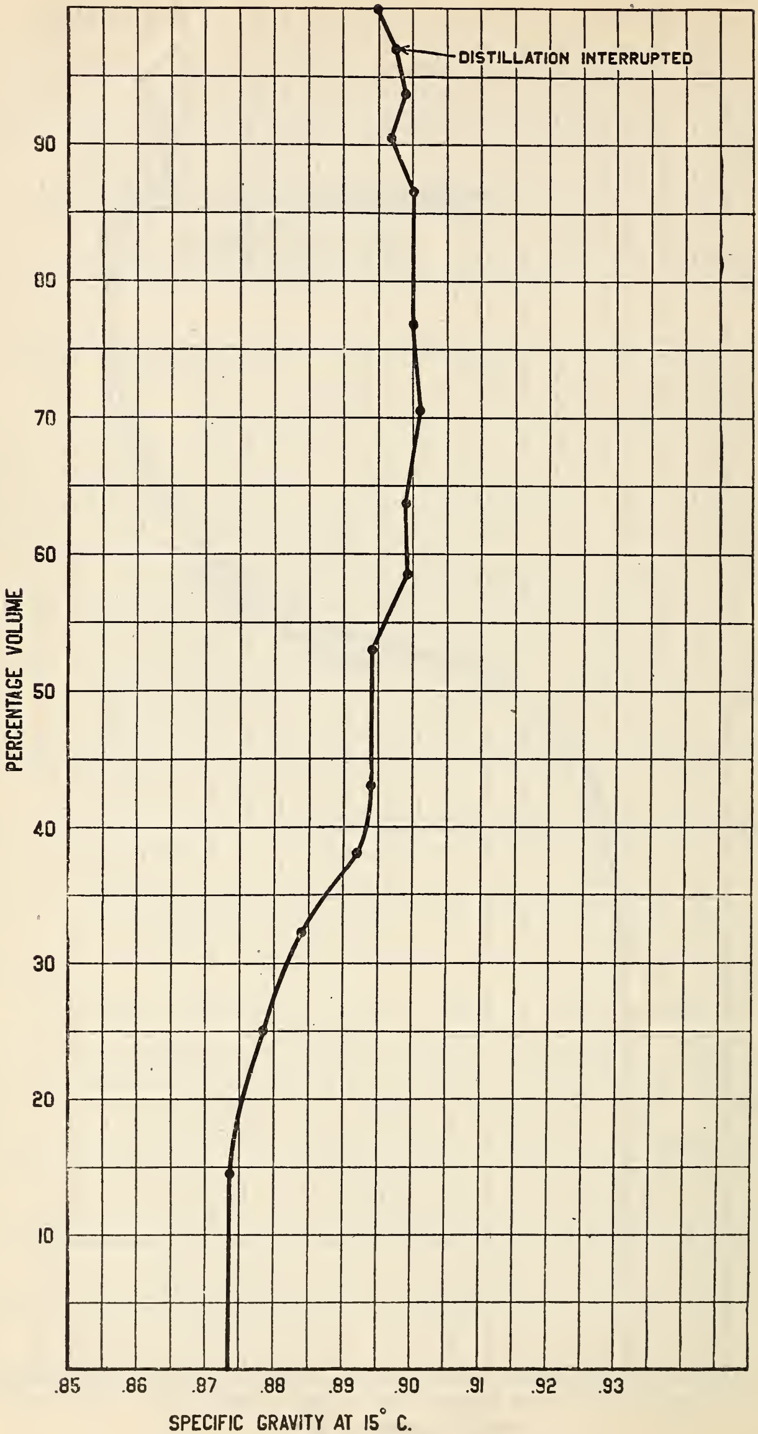

FIG. 6.—Curve showing fractionation of oil during run 20.

figure 7. This represents the gravities of different parts of the oil obtained during the distillation of chips 1 inch × $\frac{1}{4}$ inch × $\frac{1}{8}$ inch at atmospheric, at 20 pounds, and then at 40 pounds pressure. During the first of the run at atmospheric pressure the gravity gradually increased but never quite reached that of pure pine oil. By a continuous distillation at atmospheric pressure only about 50.6 per cent of the total oil could be removed, but on interrupting the distillation for about 14 hours and continuing again at atmospheric pressure, 7 per cent more of the oil was obtained, the gravity of the first part of this 7 per cent being much lower, and of the last part only slightly lower, than that of the last fraction of the continuous run. On increasing the pressure to 20 pounds about 16.8 per cent more oil was obtained, the gravity suddenly dropping and then gradually rising during the distillation of this 16.8 per cent. On increasing the pressure to 40 pounds and distilling continuously, a further yield of 19.5 per cent was obtained, the gravity of this 19.5 per cent dropping suddenly at first and then gradually rising. A similar additional yield was obtained by another interruption of the distillation, after which about 6 per cent more oil was obtained.

Here again the effect of interrupting the distillation and of increasing the pressure is very plainly shown in the increased yield of oil with gravity lower than the last fraction obtained before the conditions were changed.

This effect of increased pressure in increasing the yields is due, then, to bringing more steam and oil into contact with each other than is possible at lower pressures. This contact could result either from a penetration of the steam further into the wood or from a better flow of resin toward the surface of the wood, due to its increased fluidity. It is probable that both these have some influence, but the effect of the latter is quite certain, since, in the distillation made at high pressures, a considerable amount of rosin would collect in the bottom of the retort, or the outside of many of the chips would be coated with thin layers of rosin.

The effect due to the interruption of the distillation and continuing it again under the same conditions can not be explained so readily, but it is probably due to a slow flow of resin toward the surface or to the diffusion of the volatile oils in the resin from the interior of the chip to the resin at the surface from which the oil has been removed.

APPLICATION OF RESULTS.

In this study of the distillation of resinous wood by saturated steam the effects of different variables have been considered: (1) Size of chip, (2) pressure of steam, (3) speed of distillation, and (4) end point at which distillation is stopped, on (*a*) the yield of total oil, (*b*) the composition of the oil, and (*c*) the amount of steam required to remove the

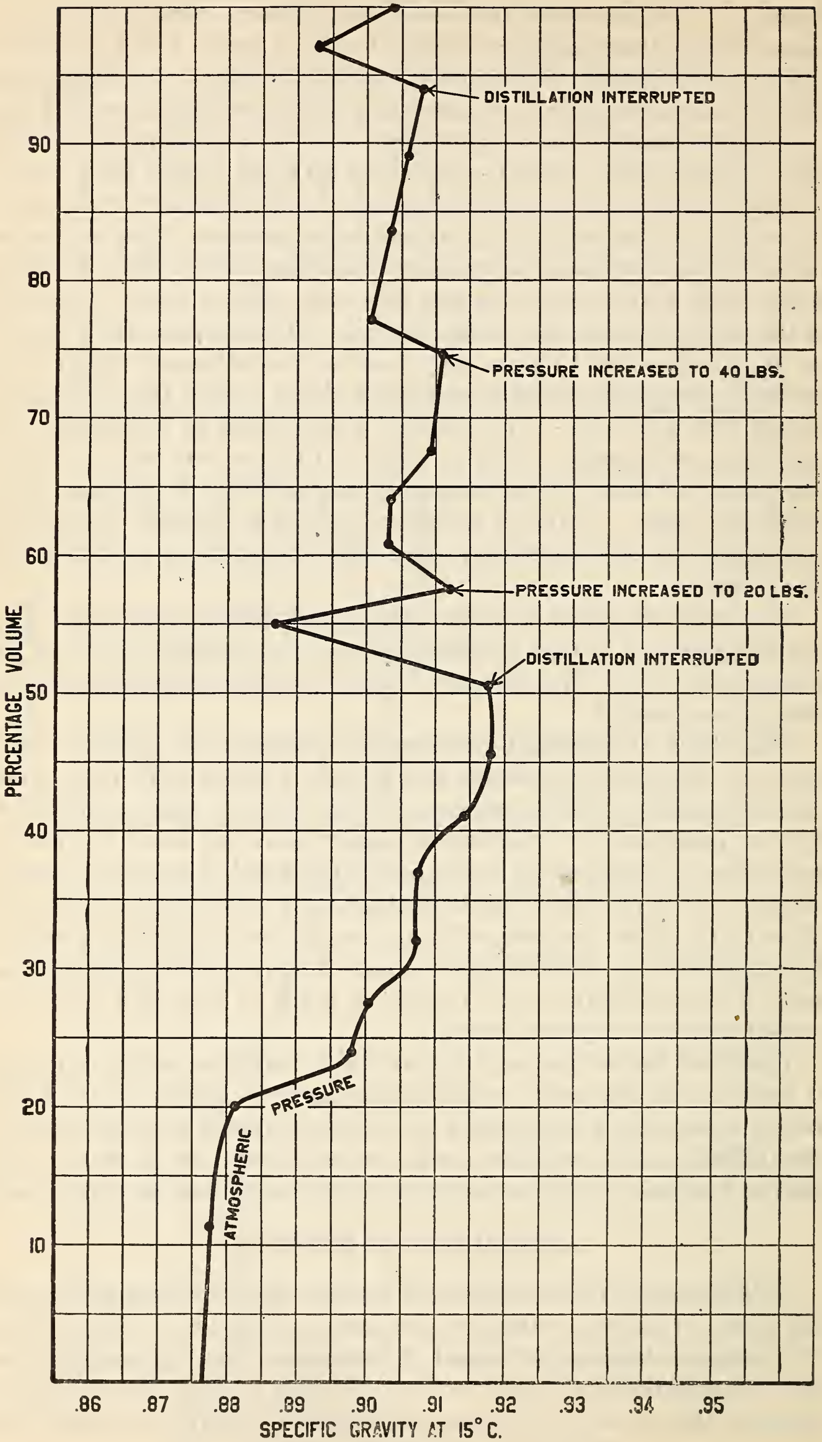

FIG. 7.—Curve showing fractionation of oil during run 7.

oil. It can be seen that there should be a certain combination of values for these variables which would give the most economical method of operation for a steam distillation plant; but there are other factors which must be taken into consideration in determining the proper combination of values. For example, the best size of the chip will not be determined entirely by the effect of size on yield and efficiency, but also by the relative costs of preparing different sized chips and the use to which the chips are to be put after steaming; the best pressure of steam will not be determined entirely by the effect of pressure on yield and efficiency, but also by the relative costs of high and low pressure steam and of apparatus for various pressures; the best speed for the distillation will not depend entirely upon the effect of speed on the yield of products and on the amount of steam required, but also upon the cost of steam and the overhead charges; the best end point at which to stop the distillation will not depend entirely upon the effect of end point on yield and efficiency, but also upon the cost of the raw material and the value of the products.

With the experimental data given, however, and with a knowledge of the various cost factors, which would naturally differ widely in different plants, it will be possible to decide readily on the most economical methods of operating.

ADDITIONAL COPIES of this publication may be procured from the SUPERINTENDENT OF DOCUMENTS, Government Printing Office, Washington, D. C., at 5 cents per copy